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Supporting Information

# Combination of four oxadiazole rings for the generation of energetic materials with high detonation performance, low sensitivity and excellent thermal stability

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## General methods

All reagents were purchased from Energy Chemical of analytical grade and were used as supplied, if not stated otherwise. $^{1}H$, $^{13}C$ spectra were recorded using a 500 MHz (Bruker AVANCE III 500) nuclear magnetic resonance spectrometer operating at 500 and 50.69 MHz, respectively. Chemical shifs in the $^{1}H$ and $^{13}C$ spectra are reported relative to $Me_4Si$ as external standards. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 10°C $min^{-1}$ in closed Al containers with a nitrogen flow of 50 ml $min^{-1}$. IR spectra were recorded using KBr pellets for solids on a Thermo Nicolet iS10 spectrometer. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer.

## X-ray Crystallography detail

A colorless plate crystal (**7**) of dimensions 0.29×0.22×0.11 $mm^3$, a colorless plate crystal (**8**·$H_2O$) of dimensions 0.25×0.22×0.17 $mm^3$, a yellow plate crystal (**9**) of dimensions 0.28×0.23×0.13 $mm^3$, a red rod crystal (**10**) of dimensions 0.25×0.21×0.17 $mm^3$, a light yellow rod crystal (**13**) of dimensions 0.29×0.18×0.15 $mm^3$, were mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) at 293 and 292 K. Corrections for Lorentz and polarization effects and for absorption (ψ scan) were applied. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares calculation on $F^2$ with SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogens were placed in calculated positions and were assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they were attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations.

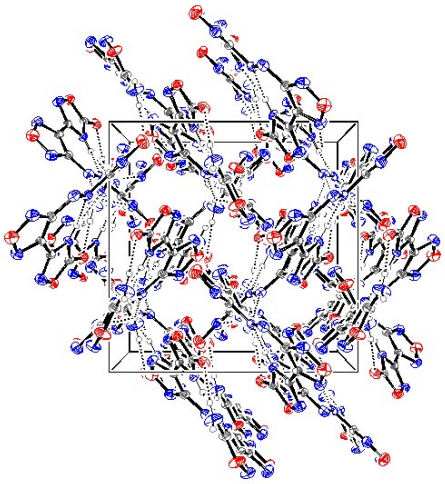


**Figure S1** Packing diagram of **7** viewed down the c axis. The dashed lines indicate hydrogen bonding.

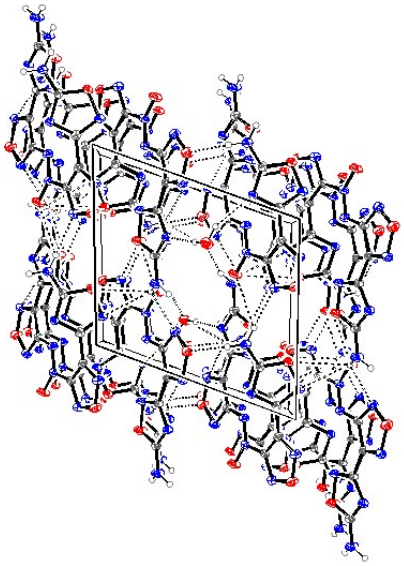


**Figure S2** Packing diagram of **8**·$H_2O$ viewed down the a axis. The dashed lines indicate hydrogen bonding.

**Table S1** Crystallographic data for **7, 8**·$H_2O$, **9, 10** and **13**

| Compound | **7** | **8**·$H_2O$ | **9** | **10** | **13** |
|---|---|---|---|---|---|
| Formula | $C_8H_3N_{11}O_5$ | $C_8H_6N_{12}O_6$ | $C_8H_{12}N_{14}O_6$ | $C_8H_8N_{12}O_6$ | $C_8H_8N_{12}O_7$ |
| $M_w$ | 333.21 | 366.25 | 400.32 | 368.26 | 384.26 |
| Crystal system | Orthorhombic | Triclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | Pbca | P-1 | C2/c | $P2_1/n$ | $P2_1/n$ |
| a [Å] | 11.5408(8) | 8.3476(6) | 15.8351(17) | 4.7289(6) | 4.5880(4) |
| b [Å] | 11.6206(8) | 9.6589(7) | 7.8057(8) | 10.5845(12) | 11.0597(10) |
| c [Å] | 18.3621(12) | 9.7715(8) | 12.8372(11) | 14.3425(19) | 14.3951(11) |
| α[°] | 90.000 | 105.546(3) | 90.000 | 90.000 | 90.000 |
| β[°] | 90.000 | 97.600(2) | 108.495(4) | 90.185 | 91.645(5) |
| γ[°] | 90.000 | 111.740(2) | 90.000 | 90.000 | 90.000 |
| V [Å$^3$] | 2462.6(3) | 681.05(9) | 1504.8(3) | 717.88(15) | 730.13(11) |
| Z | 8 | 2 | 4 | 2 | 2 |
| T [K] | 173(2) | 173(2) | 172(2) | 172(2) | 172(2) |
| λ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $\rho_{calcd}$[g cm$^{-3}$] | 1.798 | 1.786 | 1.767 | 1.704 | 1.748 |
| μ [mm$^{-1}$] | 0.153 | 0.154 | 0.151 | 0.147 | 0.153 |
| F(000) | 1344 | 372 | 824 | 376 | 392 |
| θ range[°] | 3.33-25.35 | 3.04-25.24 | 3.16-25.23 | 2.85-25.34 | 3.95-25.22 |
| Index ranges | $-13 \le h \le 13$ | $-10 \le h \le 10$ | $-18 \le h \le 18$ | $-5 \le h \le 5$ | $-5 \le h \le 5$ |
| | $-12 \le k \le 14$ | $-11 \le k \le 11$ | $-9 \le k \le 9$ | $-12 \le k \le 12$ | $-11 \le k \le 13$ |
| | $-22 \le l \le 22$ | $-11 \le l \le 11$ | $-13 \le l \le 15$ | $-17 \le l \le 17$ | $-17 \le l \le 15$ |
| Data/restraints / parameters | 2242/0/226 | 2466/2/253 | 1379/12/145 | 1312/21/130 | 1340/21/139 |
| GOF on F2 | 1.061 | 1.052 | 1.044 | 1.038 | 1.044 |
| R[$F^2 > 2\sigma(F^2)$] | 0.0558 | 0.0607 | 0.0431 | 0.0494 | 0.0440 |

**Table S2** Bond lengths (Å), bond angles (°) and dihedral angles (°) for **7**

| | | | |
|---|---|---|---|
| C1-N3 | 1.305(4) | C7-N9 | 1.302(4) |
| C1-N1 | 1.410(4) | C7-N10 | 1.364(4) |
| C1-C2 | 1.433(5) | C8-N10 | 1.315(4) |
| C2-N4 | 1.310(4) | C8-N11 | 1.316(5) |
| C2-C3 | 1.468(5) | C8-O5 | 1.334(4) |
| C3-N5 | 1.295(4) | N1-N2 | 1.242(4) |
| C3-N6 | 1.356(4) | N3-O1 | 1.355(4) |
| C4-O3 | 1.202(4) | N4-O1 | 1.379(4) |
| C4-N6 | 1.354(4) | N5-O2 | 1.421(4) |
| C4-O2 | 1.366(4) | N6-H6A | 0.83(4) |
| C5-N7 | 1.296(4) | N7-O4 | 1.374(4) |
| C5-C6 | 1.411(5) | N8-O4 | 1.389(4) |
| C5-N2 | 1.428(4) | N9-O5 | 1.430(4) |
| C6-N8 | 1.302(4) | N11-H11A | 0.84(5) |
| C6-C7 | 1.459(5) | N11-H11B | 0.90(4) |
| | | | |
| N3-C1-N1 | 114.2(3) | N10-C7-C6 | 122.8(3) |
| N3-C1-C2 | 109.5(3) | N10-C8-N11 | 128.3(3) |
| N1-C1-C2 | 136.3(3) | N10-C8-O5 | 113.5(3) |
| N4-C2-C1 | 107.6(3) | N11-C8-O5 | 118.2(3) |
| N4-C2-C3 | 116.8(3) | N2-N1-C1 | 112.7(3) |
| C1-C2-C3 | 135.6(3) | N1-N2-C5 | 110.7(3) |
| N5-C3-N6 | 112.9(3) | C1-N3-O1 | 105.4(3) |
| N5-C3-C2 | 119.0(3) | C2-N4-O1 | 105.7(3) |
| N6-C3-C2 | 128.0(3) | C3-N5-O2 | 104.2(3) |
| O3-C4-N6 | 131.1(3) | C4-N6-C3 | 107.7(3) |
| O3-C4-O2 | 122.7(3) | C4-N6-H6A | 128(2) |
| N6-C4-O2 | 106.1(3) | C3-N6-H6A | 125(2) |
| N7-C5-C6 | 109.9(3) | C5-N7-O4 | 105.1(3) |
| N7-C5-N2 | 123.9(3) | C6-N8-O4 | 105.0(3) |
| C6-C5-N2 | 126.1(3) | C7-N9-O5 | 102.1(3) |
| N8-C6-C5 | 109.0(3) | C8-N10-C7 | 101.6(3) |
| N8-C6-C7 | 121.7(3) | C8-N11-H11A | 112(3) |
| C5-C6-C7 | 129.4(3) | C8-N11-H11B | 116(3) |
| N9-C7-N10 | 116.5(3) | H11A-N11-H11B | 131(4) |
| N9-C7-C6 | 120.7(3) | N3-O1-N4 | 111.8(2) |
| N7-O4-N8 | 110.9(2) | C4-O2-N5 | 109.2(2) |
| C8-O5-N9 | 106.3(3) | | |
| | | | |
| O3-C4-O2-N5 | 177.35(3) | N1-N2-C5-C6 | 160(3) |
| O3-C4-N6-H6A | -0.06(3) | N1-N2-C5-C7 | 18.66(4) |
| O3-C4-N6-C3 | -177.78(2) | N2-C5-N7-O4 | 179.31(4) |
| H6A-N6-C4-O2 | 178.39(3) | H6A-N6-C3-N5 | -177.58(3) |

| | | | |
|---|---|---|---|
| N6-C4-O2-N5 | 1.26(3) | C4-O2-N5-C3 | 1.38(3) |
| O2-N5-C3-N6 | -0.97(2) | N5-C3-N6-C4 | 0.22(3) |
| C3-N6-C4-O2 | 0.67(3) | C2-C3-N6-C4 | -176.09(3) |
| C2-C3-N5-O2 | 175.71(3) | H6A-N6-C3-C2 | 6.11(3) |
| C3-C2-C1-N1 | -1.21(3) | C3-C2-C1-N3 | -179.96(2) |
| C3-C2-N3-O1 | -179.48(3) | C2-C1-N1-N2 | 11.70(3) |
| C2-C1-N3-O1 | -1.27(3) | C1-N3-O1-N4 | 1.19(3) |
| N3-O1-N4-C2 | -0.61(2) | O1-N4-C2-C1 | -0.19(2) |
| N4-C2-C1-N3 | 0.95(3) | O1-N3-C1-N1 | 179.68(3) |
| N4-C2-C1-N1 | 179.70(3) | N3-C1-N1-N2 | -169.60(3) |
| C1-N1-N2-C5 | 179.14(3) | N2-C5-C6-N8 | 178.93(3) |
| N2-C5-C6-C7 | -0.70(3) | C5-N7-O4-N8 | 0.65(3) |
| N7-O4-N8-C6 | -0.58(3) | O4-N8-C6-C5 | 0.28(3) |
| N8-C6-C5-C7 | 0.12(4) | C6-C5-N7-O4 | -0.46(4) |
| O4-N8-C6-C7 | 179.94(2) | N7-C5-C6-C7 | -179.51(3) |
| N8-C6-C7-N9 | -16.09(3) | N8-C6-C7-N10 | 160.91(3) |
| C5-C6-C7-N9 | 163.50(3) | C5-C6-C7-N10 | -19.50(3) |
| C6-C7-N9-O5 | 177.29(3) | C6-C7-N10-C8 | -176.64(5) |
| C7-N9-O5-C8 | -0.65(3) | N9-O5-C8-N10 | 1.03(3) |
| O5-C8-N10-C7 | 0.92(3) | C8-N10-C7-N9 | 0.48(3) |
| N10-C7-N9-O5 | 0.11(3) | C7-N10-C8-N11 | 178.33(3) |
| N9-O5-C8-N11 | -178.30(3) | O5-C8-N11-H11B | -6.22(3) |
| O5-C8-N11-H11A | 167.53(4) | N10-C8-N11-H11B | 174.56(3) |
| N10-C8-N11-H11A | -11.69(4) | | |

**Table S3** Bond lengths (Å), bond angles (°) and dihedral angles (°) for **8**·$H_2O$

| | | | |
|---|---|---|---|
| C1-N3 | 1.294(4) | C7-O5 | 1.354(4) |
| C1-C2 | 1.420(4) | C8-N10 | 1.307(4) |
| C1-N1 | 1.437(4) | C8-N11 | 1.365(4) |
| C2-N4 | 1.301(4) | N1-O1 | 1.243(3) |
| C2-C3 | 1.487(4) | N1-N2 | 1.285(3) |
| C3-N5 | 1.298(4) | N3-O2 | 1.368(3) |
| C3-N6 | 1.365(4) | N4-O2 | 1.389(3) |
| C4-N7 | 1.319(4) | N5-O3 | 1.425(3) |
| C4-N6 | 1.319(4) | N7-H7A | 0.85(4) |
| C4-O3 | 1.347(4) | N7-H7B | 0.87(4) |
| C5-N8 | 1.321(4) | N8-O4 | 1.376(3) |
| C5-N2 | 1.389(4) | N9-O4 | 1.384(3) |
| C5-C6 | 1.424(4) | N10-O5 | 1.426(3) |
| C6-N9 | 1.303(4) | N12-H12A | 0.93(4) |
| C6-C8 | 1.459(4) | N12-H12B | 0.83(4) |
| C7-N12 | 1.310(4) | O6-H6A | 0.835(18) |
| C7-N11 | 1.314(4) | O6-H6B | 0.820(18) |
| N3-C1-C2 | 110.8(3) | O1-N1-N2 | 129.2(3) |

| | | | |
|---|---|---|---|
| N3-C1-N1 | 118.8(3) | O1-N1-C1 | 117.4(2) |
| C2-C1-N1 | 130.3(3) | N2-N1-C1 | 113.3(2) |
| N4-C2-C1 | 107.8(3) | N1-N2-C5 | 116.4(2) |
| N4-C2-C3 | 119.5(3) | C1-N3-O2 | 104.6(2) |
| C1-C2-C3 | 132.7(3) | C2-N4-O2 | 105.6(2) |
| N5-C3-N6 | 118.1(3) | C3-N5-O3 | 101.5(2) |
| N5-C3-C2 | 119.5(3) | C4-N6-C3 | 100.4(3) |
| N6-C3-C2 | 122.4(3) | C4-N7-H7A | 120(2) |
| N7-C4-N6 | 129.3(3) | C4-N7-H7B | 118(2) |
| N7-C4-O3 | 117.1(3) | H7A-N7-H7B | 121(3) |
| N6-C4-O3 | 113.7(3) | C5-N8-O4 | 104.4(2) |
| N8-C5-N2 | 128.0(3) | C6-N9-O4 | 105.3(2) |
| N8-C5-C6 | 109.4(3) | C8-N10-O5 | 101.6(2) |
| N2-C5-C6 | 122.6(3) | C7-N11-C8 | 101.8(2) |
| N9-C6-C5 | 108.9(3) | C7-N12-H12A | 121(2) |
| N9-C6-C8 | 119.5(3) | C7-N12-H12B | 119(2) |
| C5-C6-C8 | 131.6(3) | H12A-N12-H12B | 117(3) |
| N12-C7-N11 | 129.1(3) | N3-O2-N4 | 111.3(2) |
| N12-C7-O5 | 118.2(3) | C4-O3-N5 | 106.4(2) |
| N11-C7-O5 | 112.8(3) | N8-O4-N9 | 111.9(2) |
| N10-C8-N11 | 117.0(3) | C7-O5-N10 | 106.8(2) |
| N10-C8-C6 | 121.0(3) | H6A-O6-H6B | 107(4) |
| N11-C8-C6 | 122.0(3) | | |
| | | | |
| H12A-N12-C7-N11 | -7.88(3) | H12A-N12-C7-O5 | 173.90(3) |
| H12B-N12-C7-N11 | -168.96(4) | H12B-N12-C7-O5 | 12.82(3) |
| N12-C7-N11-C8 | -179.78(4) | N12-C7-O5-N10 | -179.95(2) |
| C7-N11-C8-N10 | 0.93(3) | N11-C8-N10-O5 | -0.04(2) |
| C8-N10-O5-C7 | -0.85(3) | N10-O5-C7-N11 | 1.54(2) |
| O5-C7-N11-C8 | -1.48(3) | C6-C8-N11-C7 | -177.37(3) |
| C6-C8-N10-O5 | 174.12(5) | C6-C6-C8-N11 | 173.09(3) |
| C5-C6-C8-N10 | -5.13(4) | N9-C6-C8-N10 | 177.36(3) |
| N9-C6-C8-N11 | -4.41(3) | N8-C5-C6-C8 | -177.68(5) |
| O4-N9-C6-C8 | 178.40(3) | C6-C5-N8-O4 | -0.40(3) |
| C5-N8-O4-N9 | -0.66(3) | N8-O4-N9-C6 | 0.66(3) |
| O4-N9-C6-C5 | 0.38(4) | N9-C6-C5-N8 | 0.02(4) |
| N2-C5-C6-C8 | 3.11(4) | N2-C5-C6-N9 | -177.68(3) |
| N2-C5-N8-O4 | 178.75(4) | N1-N2-C5-C6 | -176.91(3) |
| N1-N2-C5-N8 | 4.04(3) | C5-N2-N1-O1 | -179.94(3) |
| C5-N2-N1-C1 | -176.13(3) | O1-N1-C1-C2 | 172.05(5) |
| O1-N1-C1-C2 | 172.05(3) | O1-N1-C1-N3 | 165.78(3) |
| N1-C1-N3-O2 | -177.42(3) | N1-C1-C2-N4 | 176.84(3) |
| N1-C1-C2-C3 | -5.41(3) | C1-C2-N4-O2 | 0.42(3) |
| C2-N4-O2-N4 | 0.34(3) | N4-O2-N3-C1 | 0.10(3) |

| | | | |
|---|---|---|---|
| O2-N3-C1-C2 | 0.16(3) | N3-C1-C2-C3 | 177.37(3) |
| O2-N4-C2-C3 | -177.69(3) | C1-C2-C3-N6 | -65.32(3) |
| C1-C2-C3-N5 | 117.24(2) | N4-C2-C3-N6 | 112.23(3) |
| N4-C2-C3-N5 | -65.21(2) | C2-C3-N6-C4 | -177.14(3) |
| C2-C3-N5-O3 | 177.94(2) | C3-N5-O3-C4 | -0.94(4) |
| N5-O3-C4-N6 | 1.28(3) | O3-C4-N6-C3 | -0.99(4) |
| C4-N6-C3-N5 | 0.33(3) | N6-C3-N5-O3 | 0.39(3) |
| N5-O2-C4-N7 | -177.71(3) | C3-N6-C4-N7 | 177.94(3) |
| N6-C4-N7-H7B | 3.95(3) | N6-C4-N7-H7A | 179.14(2) |
| O3-C4-N7-H7A | -2.06(3) | O3-C4-N7-H7B | -177.25(3) |

**Table S4** Bond lengths (Å), bond angles (°) and dihedral angles (°) for **9**

| | | | |
|---|---|---|---|
| C1-N2 | 1.312(3) | N1-H1A | 0.834(17) |
| C1-N1 | 1.357(3) | N2-O1 | 1.403(3) |
| C1-C2 | 1.427(3) | N3-O1 | 1.369(2) |
| C2-N3 | 1.298(3) | N4-O2 | 1.413(2) |
| C2-C3 | 1.462(3) | N6-N7 | 1.441(3) |
| C3-N4 | 1.307(3) | N6-H6A | 0.944(14) |
| C3-N5 | 1.356(3) | N6-H6B | 0.884(14) |
| C4-O3 | 1.236(3) | N6-H6C | 0.887(14) |
| C4-N5 | 1.336(3) | N7-H7A | 0.893(17) |
| C4-O2 | 1.378(3) | N7-H7B | 0.899(17) |
| N1-N1A | 1.391(4) | | |
| | | | |
| N2-C1-N1 | 125.3(2) | N3-C2-C1 | 109.3(2) |
| N2-C1-C2 | 109.1(2) | N3-C2-C3 | 122.7(2) |
| N1-C1-C2 | 125.6(2) | C1-C2-C3 | 128.0(2) |
| N4-C3-N5 | 116.8(2) | O3-C4-N5 | 130.4(2) |
| N4-C3-C2 | 118.6(2) | O3-C4-O2 | 118.93(19) |
| N5-C3-C2 | 124.6(2) | N5-C4-O2 | 110.64(18) |
| C1-N1-N1A | 118.4(2) | C1-N1-H1A | 122(2) |
| N1A-N1-H1A | 118(2) | C1-N2-O1 | 104.45(18) |
| C2-N2-O1 | 105.91(18) | C3-N4-O2 | 102.58(17) |
| C4-N5-C3 | 102.82(18) | N7-N6-H6A | 104.7(12) |
| N7-N6-H6B | 110.7(13) | H6B-N6-H6C | 113.6(16) |
| H6A-N6-H6B | 108.6(16) | N6-N7-H7A | 106.1(18) |
| N7-N6-H6C | 109.7(13) | N6-N7-H7B | 99.8(18) |
| H6A-N6-H6C | 109.2(15) | H7A-N7-H7B | 114(3) |
| N3-O1-N2 | 111.16(16) | C4-O2-N4 | 107.16(16) |
| | | | |
| O3-C4-N5-C3 | 179.92(3) | O3-C4-O2-N4 | -179.66(3) |
| C4-N5-C3-N4 | -0.54(4) | N5-C3-N4-O2 | 0.56(2) |
| C3-N4-O2-C4 | -0.34(3) | N4-O2-C4-C5 | 0.04(3) |
| O2-C4-N5-C3 | 0.27(3) | C2-C3-N5-C4 | -179.86(3) |

| | | | |
|---|---|---|---|
| C2-C3-N4-O2 | 179.91(5) | N3-C2-C3-N4 | -166.50(3) |
| N3-C2-C3-N5 | 12.80(2) | C1-C2-C3-N5 | -167.89(3) |
| C1-C2-C3-N4 | 12.81(3) | C2-N3-O1-N2 | 1.63(4) |
| N3-O1-N2-C1 | -1.76(3) | O1-N2-C1-C2 | 1.17(4) |
| N2-C1-C2-N3 | -0.23(3) | C1-C2-N3-O1 | -0.86(3) |
| N1-C1-C2-N3 | 179.25(4) | N1-C1-C2-C3 | -0.13(3) |
| N1-C1-N2-O1 | -178.31(4) | H1A-N1-C1-N2 | -173.44(3) |
| H1A-N1-C1-C2 | 7.16(3) | H1A-N1-N1A-C1A | -90.53(3) |
| H1A-N1-N1A-H1AA | 75.18(3) | C2-C1-N1-N1A | 172.28(3) |
| N2-C1-N1-N1A | -8.32(2) | C1-N1-N1A-CA | 103.76(2) |
| C1-N1-N1A-H1AA | -90.53(2) | H6A-N6-N7-H7A | -176.07(4) |
| H6A-N6-N7-H7B | -57.45(3) | H6B-N6-N7-H7A | -59.19(3) |
| H6B-N6-N7-H7B | 59.42(3) | H6C-N6-N7-H7A | 66.93(3) |
| H6C-N6-N7-H7B | -174.46(3) | | |

**Table S5** Bond lengths (Å), bond angles (°) and dihedral angles (°) for **10**

| | | | |
|---|---|---|---|
| C1-N2 | 1.304(3) | C3-N4 | 1.313(3) |
| C1-N1 | 1.418(3) | C3-N5 | 1.355(3) |
| C1-C2 | 1.423(3) | C4-O3 | 1.237(3) |
| C2-N3 | 1.311(3) | C4-N5 | 1.334(3) |
| C2-C3 | 1.457(3) | C4-O2 | 1.381(3) |
| N1-N1A | 1.250(4) | N6-H6A | 0.921(15) |
| N2-O1 | 1.376(3) | N6-H6B | 0.915(15) |
| N3-O1 | 1.385(3) | N6-H6C | 0.917(15) |
| N4-O2 | 1.421(3) | N6-H6D | 0.913(15) |
| | | | |
| N2-C1-N1 | 124.9(2) | N4-C3-N5 | 116.7(2) |
| N2-C1-C2 | 109.8(2) | N4-C3-C2 | 121.6(2) |
| N1-C1-C2 | 125.3(2) | N5-C3-C2 | 121.7(2) |
| N3-C2-C1 | 108.5(2) | O3-C4-N5 | 129.8(2) |
| N3-C2-C3 | 119.8(2) | O3-C4-O2 | 119.6(2) |
| C1-C2-C3 | 131.6(2) | N5-C4-O2 | 110.5(2) |
| N1A-N1-C1 | 112.0(3) | C4-N5-C3 | 103.3(2) |
| C1-N2-O1 | 105.0(2) | H6A-N6-H6B | 109.6(14) |
| C2-N3-O1 | 105.2(2) | H6A-N6-H6C | 108.9(15) |
| C3-N4-O2 | 102.32(19) | H6B-N6-H6C | 109.3(14) |
| H6A-N6-H6D | 108.7(14) | N2-O1-N3 | 111.44(18) |
| H6B-N6-H6D | 110.7(15) | C4-O2-N4 | 107.16(18) |
| H6C-N6-H6D | 109.6(15) | | |
| | | | |
| O3-C4-N5-C3 | -176.52(3) | O3-C4-O2-N4 | -176.78(3) |
| C4-N5-C3-N4 | -1.12(4) | N5-C3-N4-O2 | 0.21(3) |
| C3-N4-O2-C4 | 0.78(4) | N4-O2-C4-C5 | -1.53(2) |
| O2-C4-C5-C3 | -1.57(3) | C2-C3-N5-C4 | -179.43(3) |

| | | | |
|---|---|---|---|
| C2-C3-N4-O2 | -179.75(4) | N3-C2-C3-N4 | -175.78(2) |
| N3-C2-C3-N5 | 4.70(3) | C1-C2-C3-N5 | -173.92(3) |
| C1-C2-C3-N4 | -5.60(2) | N2-C1-C2-C3 | -179.50(2) |
| O1-N3-C2-C3 | -179.47(3) | N1-C1-C2-C3 | 1.42(5) |
| C2-N3-O1-N2 | -1.03(3) | N3-O1-N2-C1 | -0.04(3) |
| O1-N2-C1-C2 | -1.04(5) | N2-C1-C2-N3 | 1.76(5) |
| C1-C2-N3-O1 | 1.62(3) | N1-C1-N2-O1 | -179.13(3) |
| N1A-N1-C1-N2 | -21.82(3) | N1A-N1-C1-C2 | 160.38(3) |
| C1A-N1A-N1-C1 | 0 | | |

**Table S6** Bond lengths (Å), bond angles (°) and dihedral angles (°) for **13**

| | | | |
|---|---|---|---|
| C1-N2 | 1.298(3) | C4-O4 | 1.231(3) |
| C1-C2 | 1.419(3) | C4-N5 | 1.339(3) |
| C1-N1 | 1.419(3) | C4-O3 | 1.380(3) |
| C2-N3 | 1.308(3) | N1-O1 | 1.203(4) |
| C2-C3 | 1.461(3) | N1-N1A | 1.273(4) |
| C3-N4 | 1.310(3) | N2-O2 | 1.371(3) |
| C3-N5 | 1.351(3) | N3-O2 | 1.383(2) |
| N4-O3 | 1.421(2) | N6-H6C | 0.914(14) |
| N6-H6A | 0.916(14) | N6-H6D | 0.910(14) |
| N6-H6B | 0.927(14) | | |
| | | | |
| N2-C1-C2 | 110.5(2) | N4-C3-C2 | 122.00(19) |
| N2-C1-N1 | 122.7(2) | N5-C3-C2 | 120.86(19) |
| C2-C1-N1 | 126.5(2) | O4-C4-N5 | 130.0(2) |
| N3-C2-C1 | 107.88(19) | O4-C4-O3 | 119.5(2) |
| N3-C2-C3 | 120.31(19) | N5-C4-O3 | 110.45(18) |
| C1-C2-C3 | 131.8(2) | O1-N1-N1A | 130.7(3) |
| N4-C3-N5 | 117.12(19) | O1-N1-C1 | 113.4(2) |
| N1A-N1-C1 | 115.6(2) | C3-N4-O3 | 102.19(16) |
| C1-N2-O2 | 104.68(18) | C4-N5-C3 | 103.04(18) |
| C2-N3-O2 | 105.51(18) | H6A-N6-H6B | 107.5(13) |
| H6A-N6-H6C | 110.4(14) | H6B-N6-H6D | 109.9(14) |
| H6B-N6-H6C | 108.3(14) | H6C-N6-H6D | 110.4(14) |
| H6A-N6-H6D | 110.3(14) | N2-O2-N3 | 111.39(16) |
| C4-O3-N4 | 107.19(16) | | |
| | | | |
| O4-C4-N5-C3 | 176.87(3) | O4-C4-O3-N4 | -177.29(3) |
| C4-N5-C3-N4 | 1.15(2) | N5-C3-N4-O3 | -0.49(3) |
| C3-N4-O3-C4 | -0.37(2) | N4-O3-C4-N5 | -0.17(4) |
| O3-C4-N5-C3 | 1.31(3) | N3-C2-C3-N5 | -1.66(3) |
| N3-C2-C3-N4 | -179.86(3) | C1-C2-C3-N4 | -1.23(2) |
| C1-C2-C3-N5 | 176.98(3) | C2-N3-O2-N2 | -0.71(3) |
| N3-O2-N2-C1 | 0.08(3) | O2-N2-C1-C2 | 0.54(3) |

| | | | |
|---|---|---|---|
| N2-C1-C2-N3 | -1.02(4) | C1-C2-N3-O2 | 0.99(3) |
| N1-C1-C2-C3 | 5.81(5) | N1-C1-N2-O2 | 175.20(2) |
| O1-N1-C1-C2 | -49.56(3) | O1-N1-C1-N2 | 124.21(3) |
| O1-N1-N1A-O1A | 0 | O1-N1-N1A-C1 | 7.67(4) |
| C1-N1-N1A-C1A | 0 | C2-C1-N1-N1A | -137.77(3) |

## Hydrogen bonds for 8.$H_2O$, 9, 10 and 13

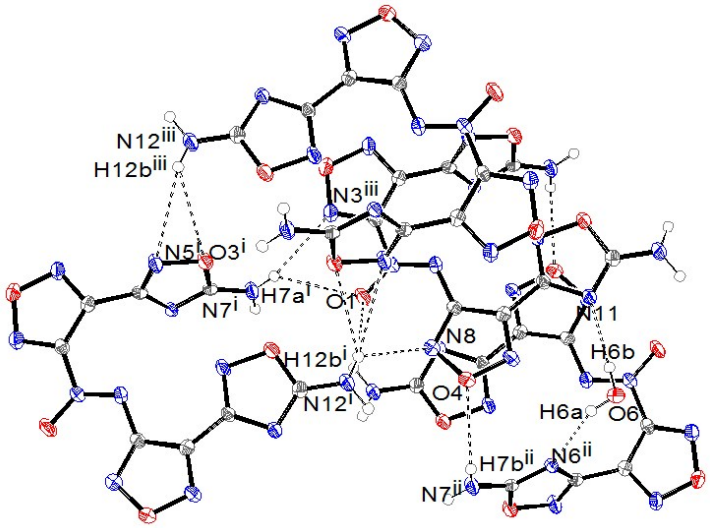



**Figure S3** Hydrogen bonds for **8.**$H_2O$

**Table S7** Hydrogen bonds for **8**.$H_2O$

| D-H···A | D-H/Å | H···A/Å | D···A/Å | D-H···A/° |
|---|---|---|---|---|
| O6-H6b···N11 | 0.816 | 2.092 | 2.907 | 175.847 |
| O6-H6a···N6$^{ii}$ | 0.838 | 2.199 | 2.985 | 156.123 |
| N12$^{i}$-H12b$^{i}$···N8 | 0.826 | 2.493 | 3.049 | 125.597 |
| N7$^{i}$-N7a$^{i}$···O1 | 0.844 | 2.649 | 3.283 | 132.899 |
| N12$^{i}$-H12b$^{i}$···O1 | 0.826 | 2.792 | 3.494 | 144.007 |
| N7$^{i}$-H7a$^{i}$···N3$^{iii}$ | 0.844 | 2.464 | 3.224 | 150.272 |
| N7$^{ii}$-H7b$^{ii}$···O4 | 0.873 | 2.523 | 3.097 | 123.983 |
| N12$^{iii}$-H12b$^{iii}$···N5$^{i}$ | 0.826 | 2.823 | 3.527 | 144.205 |
| N12$^{iii}$-H12b$^{iii}$···O3$^{i}$ | 0.826 | 2.899 | 3.413 | 122.382 |

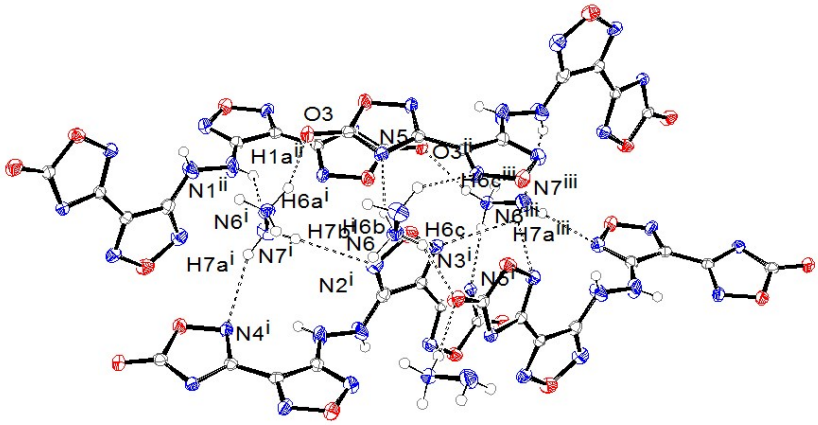



**Figure S4** Hydrogen bonds for **9**

**Table S8** Hydrogen bonds for **9**

| D-H···A | D-H/Å | H···A/Å | D···A/Å | D-H···A/° |
|---|---|---|---|---|
| N6-H6b···N5 | 0.884 | 2.024 | 2.858 | 156.839 |

| | | | | |
|---|---|---|---|---|
| N7$^{i}$-H7a$^{i}$···N4$^{i}$ | 0.894 | 2.420 | 3.250 | 154.550 |
| N7$^{i}$-H7b$^{i}$···N2$^{i}$ | 0.890 | 2.571 | 3.467 | 175.110 |
| N6$^{i}$-H6a$^{i}$···O3 | 0.944 | 1.853 | 2.715 | 150.575 |
| N1$^{ii}$-H1a$^{ii}$···N7$^{i}$ | 0.833 | 2.395 | 3.048 | 135.782 |
| N7$^{iii}$-H7a$^{iii}$···N3$^{i}$ | 0.894 | 2.778 | 3.376 | 125.438 |
| N6$^{iii}$-H6c$^{iii}$···O3$^{ii}$ | 0.888 | 2.001 | 2.792 | 147.633 |

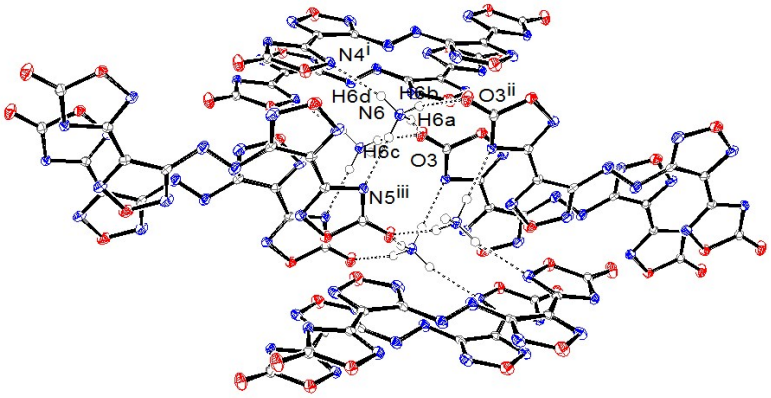



**Figure S5** Hydrogen bonds for **10**

**Table S9** Hydrogen bonds for **10**

| D-H···A | D-H/Å | H···A/Å | D···A/Å | D-H···A/° |
|---|---|---|---|---|
| N6-H6a···O3 | 0.922 | 1.897 | 2.805 | 167.616 |
| N6-H6b···O3$^{ii}$ | 0.916 | 1.963 | 2.864 | 167.479 |
| N6-H6c···N5$^{iii}$ | 0.916 | 2.008 | 2.922 | 175.736 |
| N6-H6d···N4$^{i}$ | 0.913 | 2.113 | 3.013 | 167.924 |

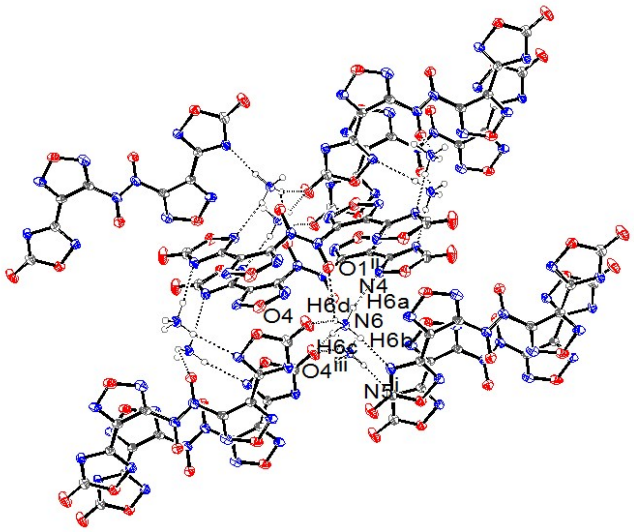



**Figure S6** Hydrogen bonds for **13**

**Table S10** Hydrogen bonds for **13**

| D-H···A | D-H/Å | H···A/Å | D···A/Å | D-H···A/° |
|---|---|---|---|---|
| N6-H6a···N4 | 0.916 | 2.253 | 3.160 | 170.149 |

| | | | | |
|---|---|---|---|---|
| N6-H6b···N5[i] | 0.927 | 1.972 | 2.897 | 175.149 |
| N6-H6c···O4[iii] | 0.913 | 1.912 | 2.815 | 169.725 |
| N6-H6d···O1[ii] | 0.910 | 2.554 | 3.159 | 124.387 |
| N6-H6d···O4 | 0.910 | 1.984 | 2.865 | 162.438 |

## DSC thermogram of related compounds

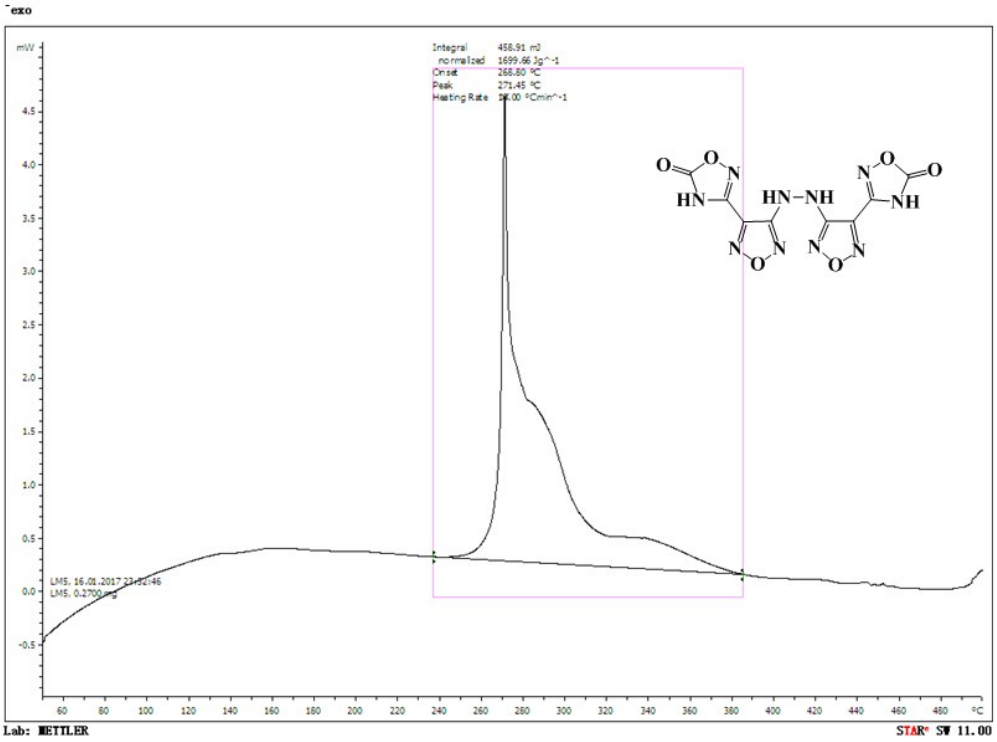



**Figure S7** DSC plot of compound **2**

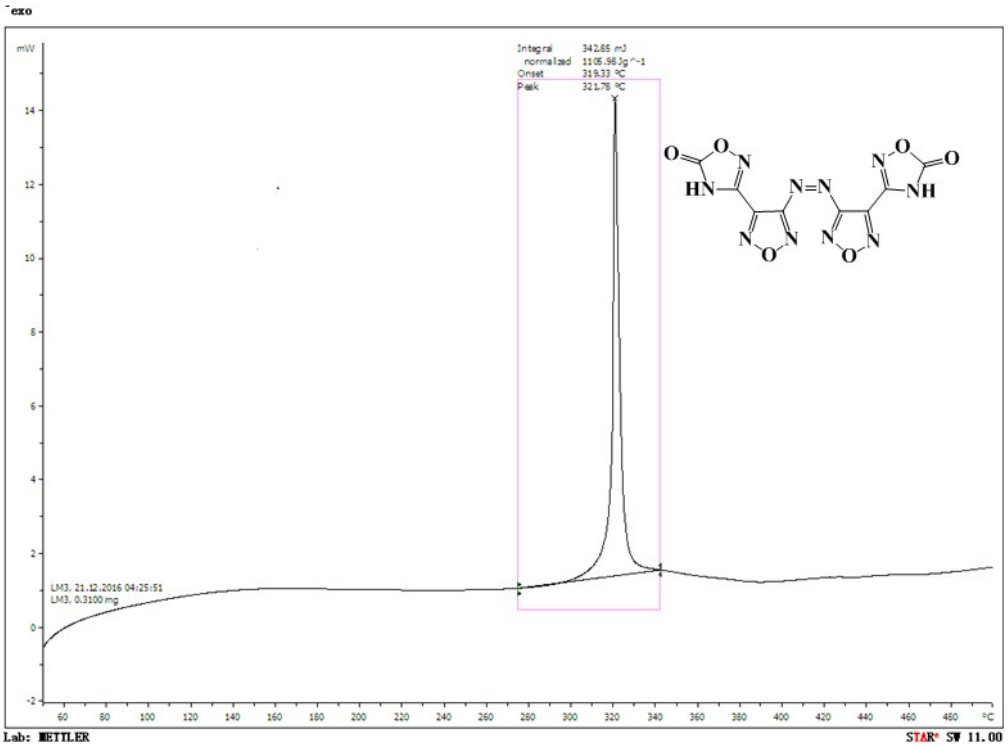



**Figure S8** DSC plot of compound **3**

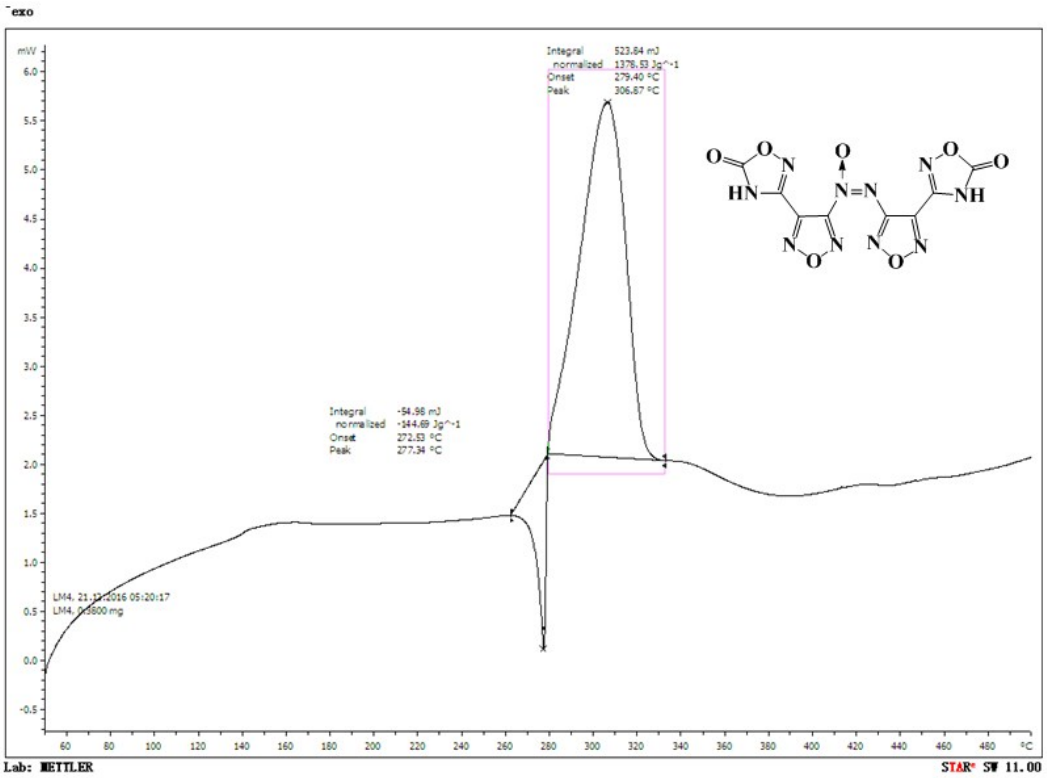



**Figure S9** DSC plot of compound **4**

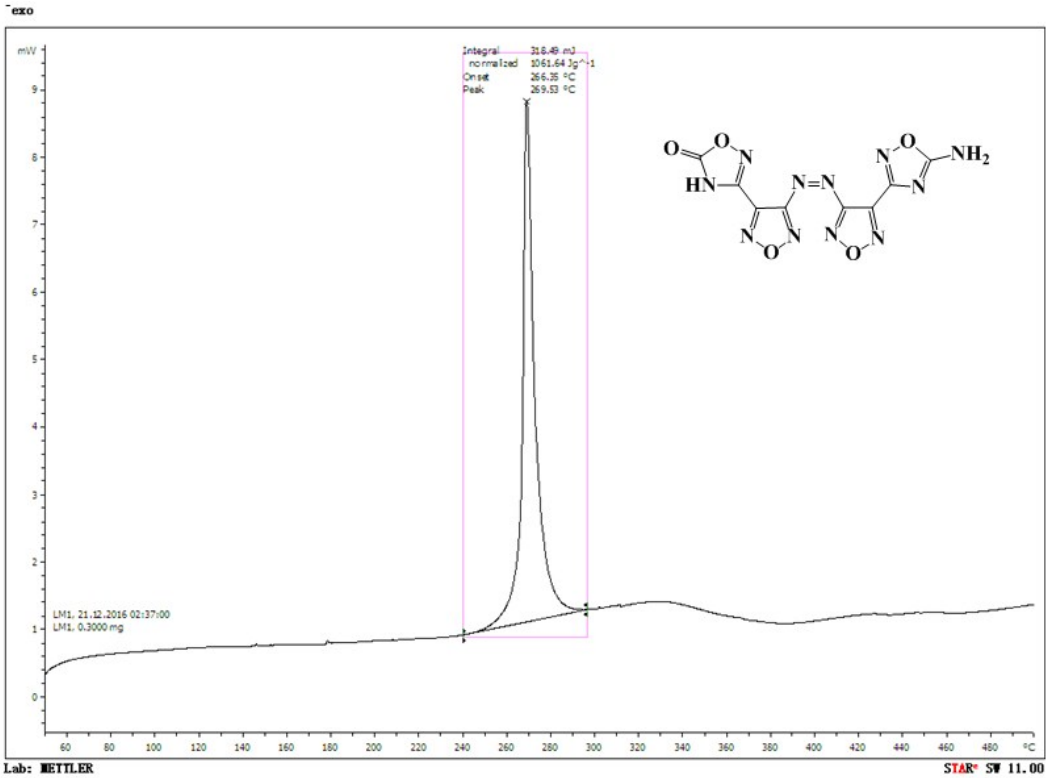



**Figure S10** DSC plot of compound **7**

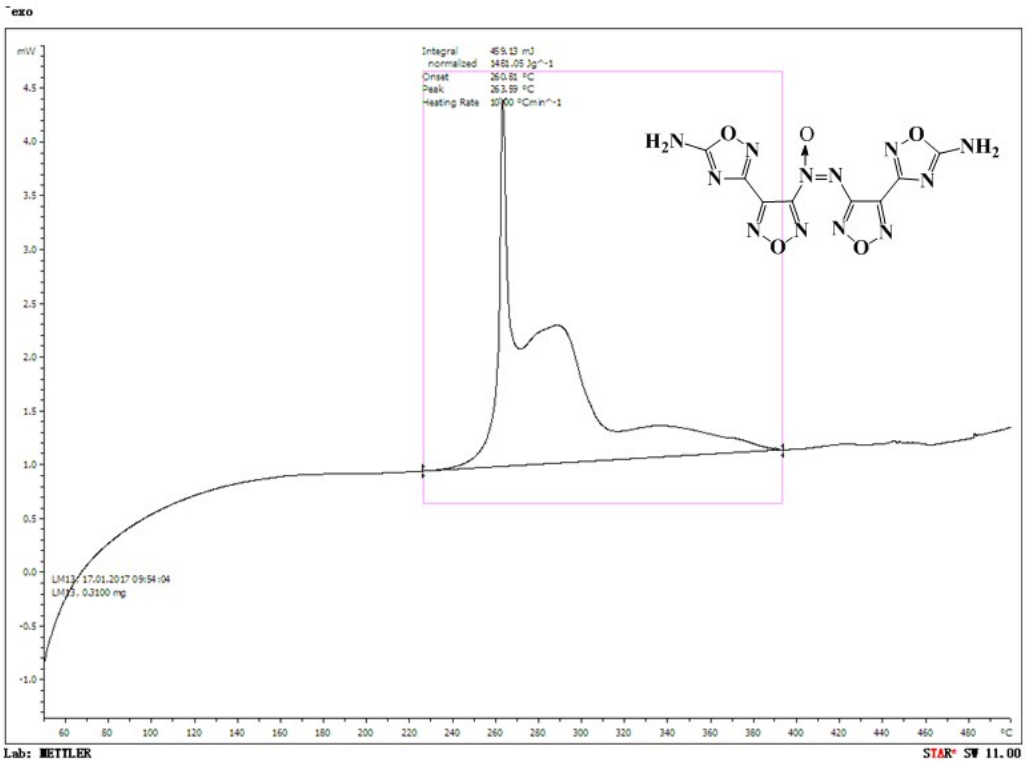



**Figure S11** DSC plot of compound **8**

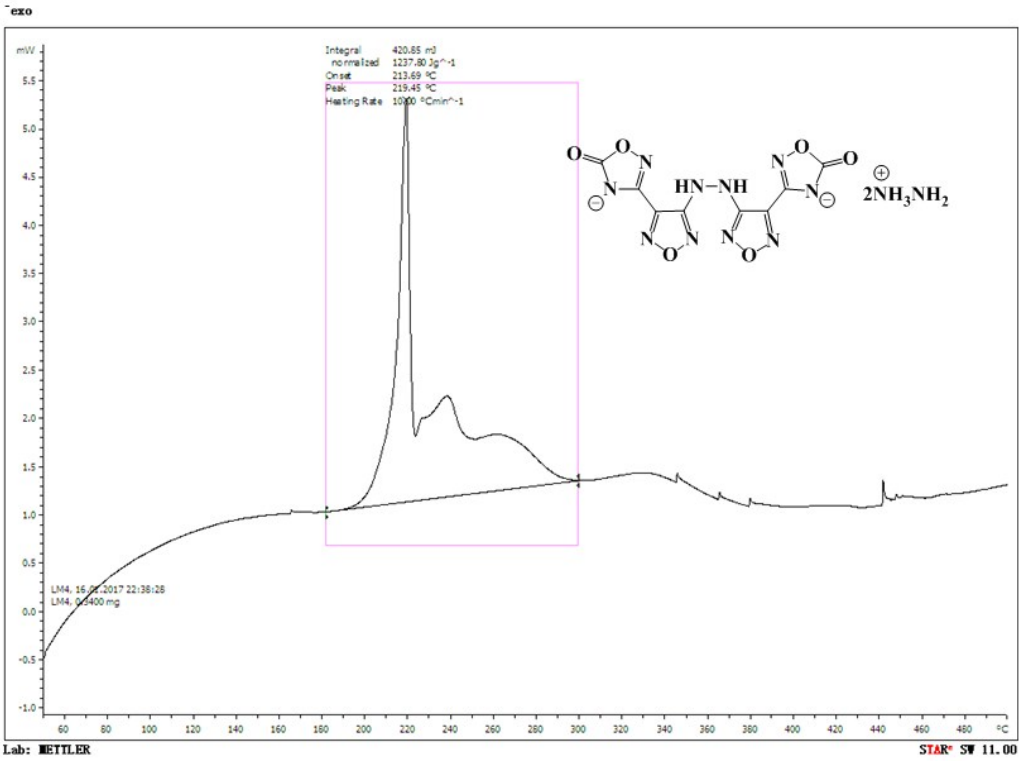



**Figure S12** DSC plot of compound **9**

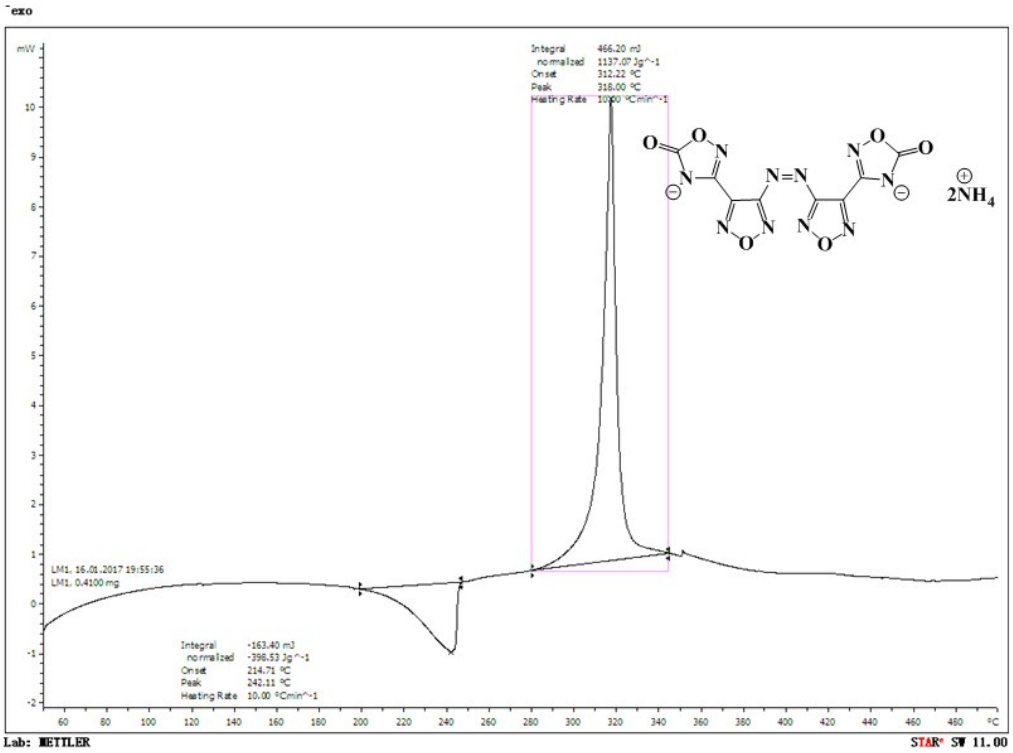



**Figure S13** DSC plot of compound **10**

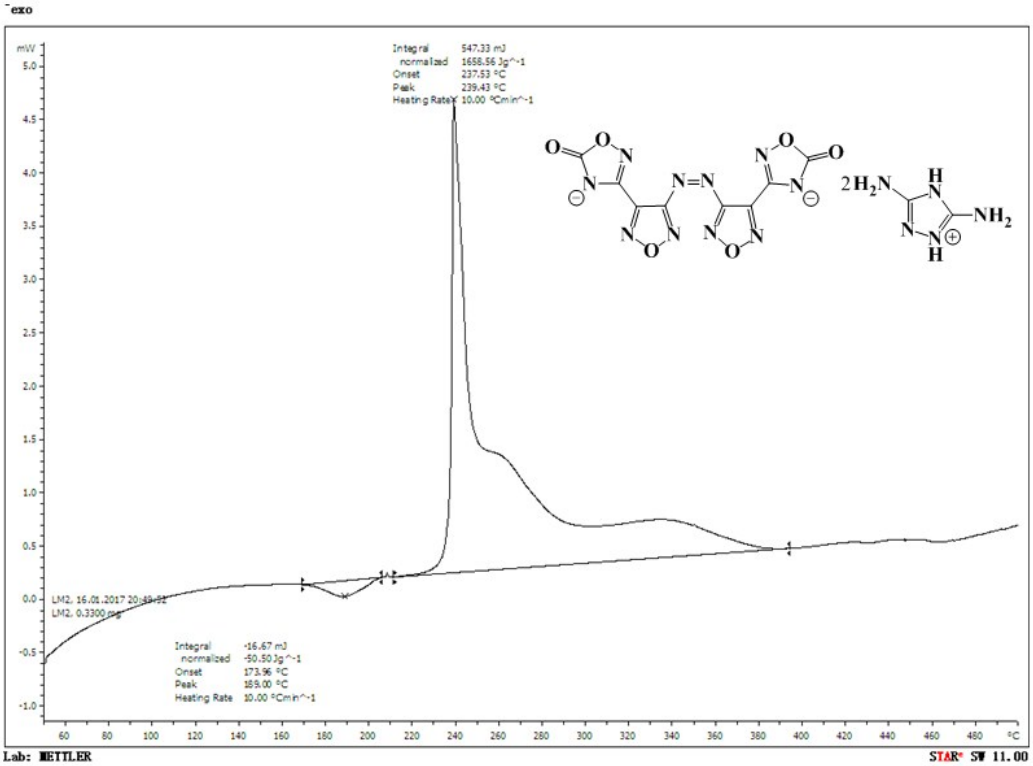



**Figure S14** DSC plot of compound **11**

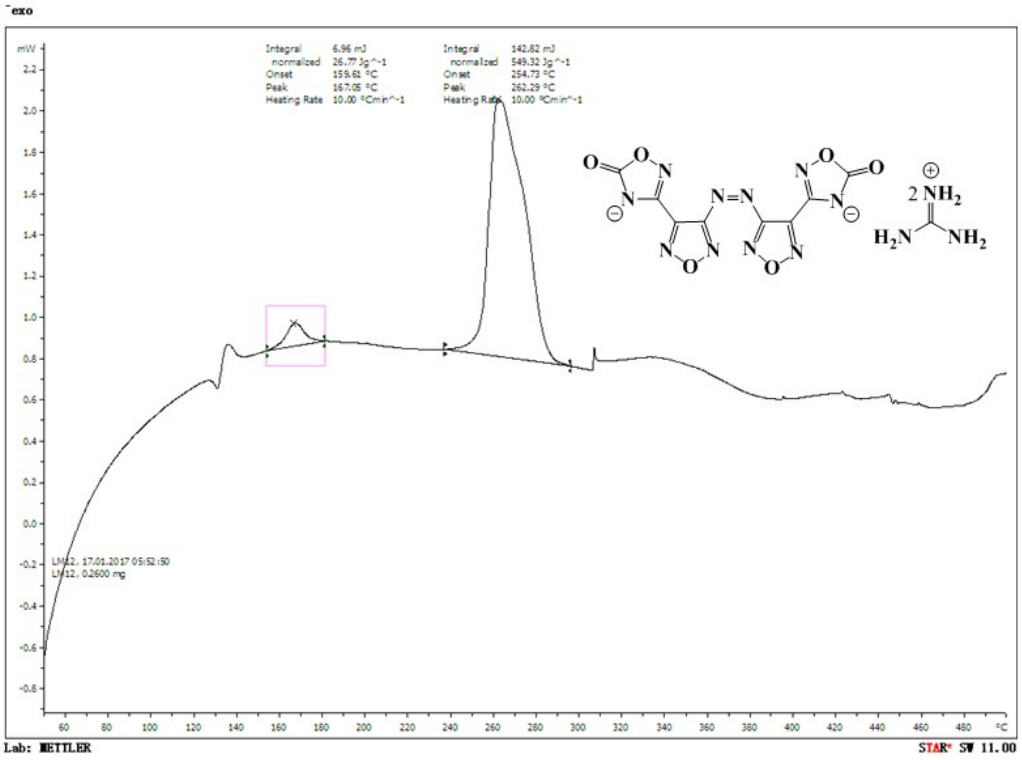



**Figure S15** DSC plot of compound **12**

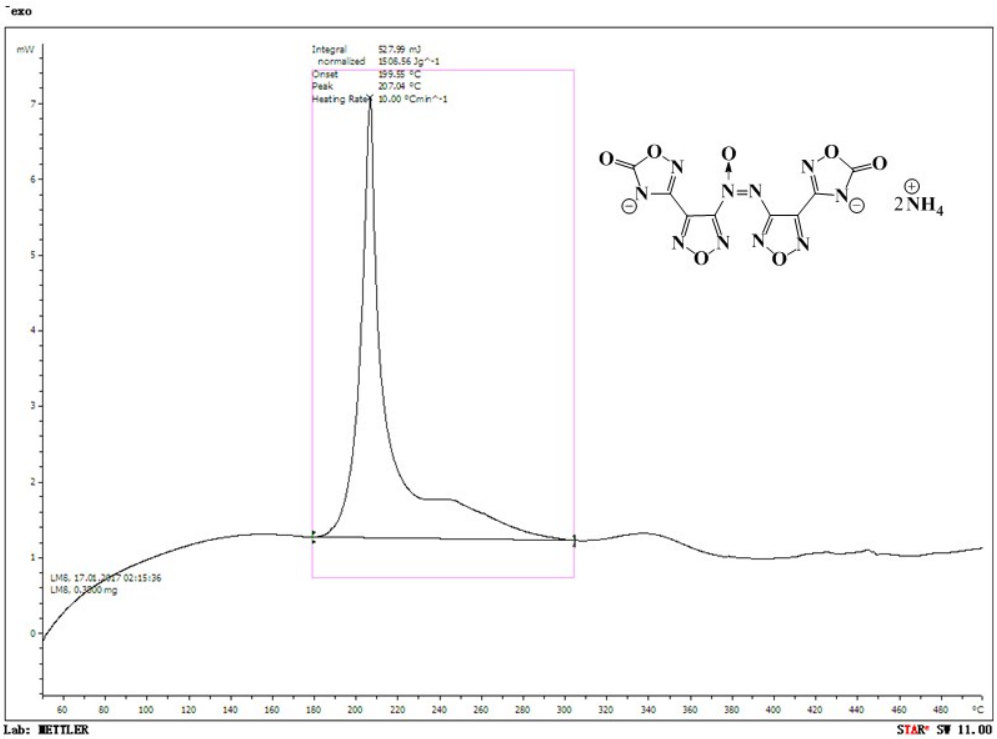



**Figure S16** DSC plot of compound **13**

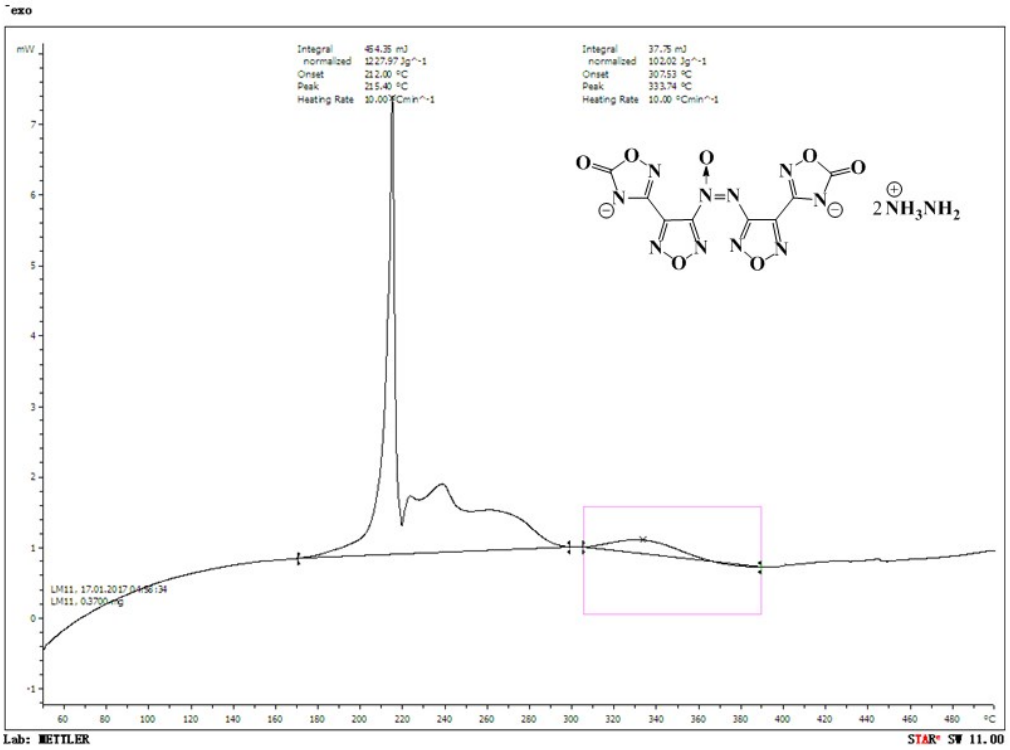



**Figure S17** DSC plot of compound **14**

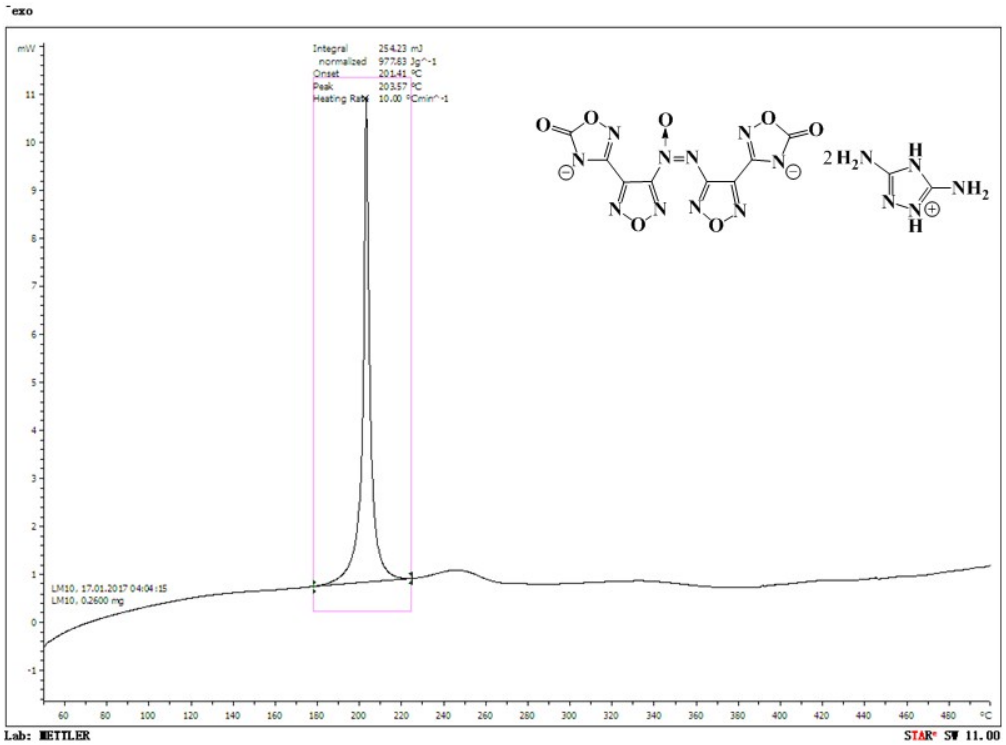



**Figure S18** DSC plot of compound **15**

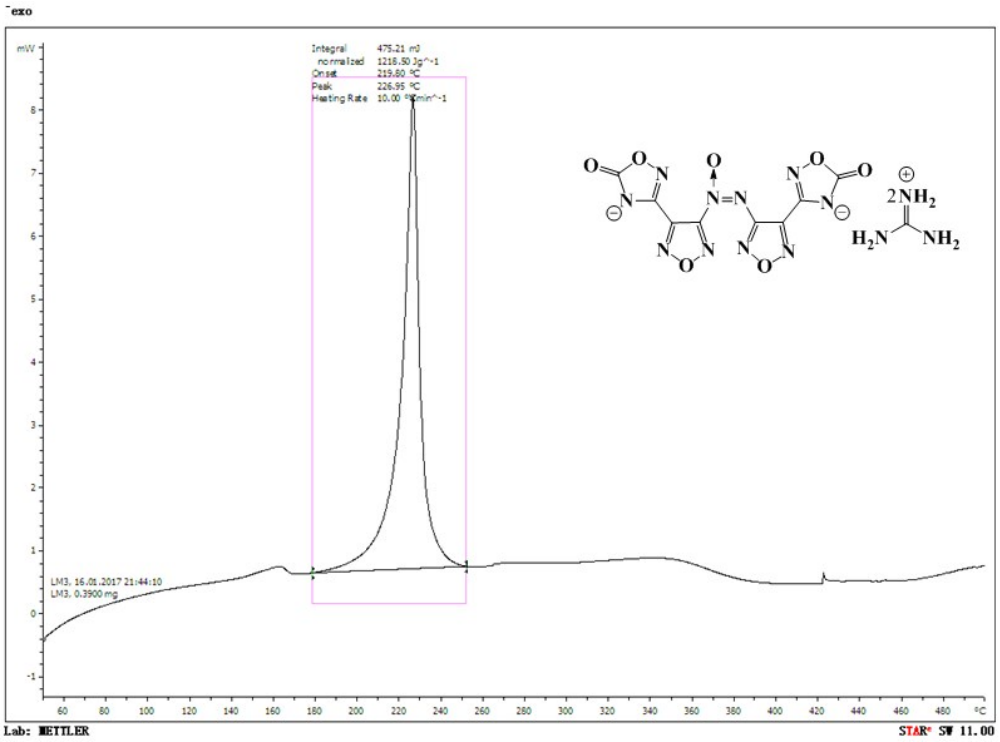
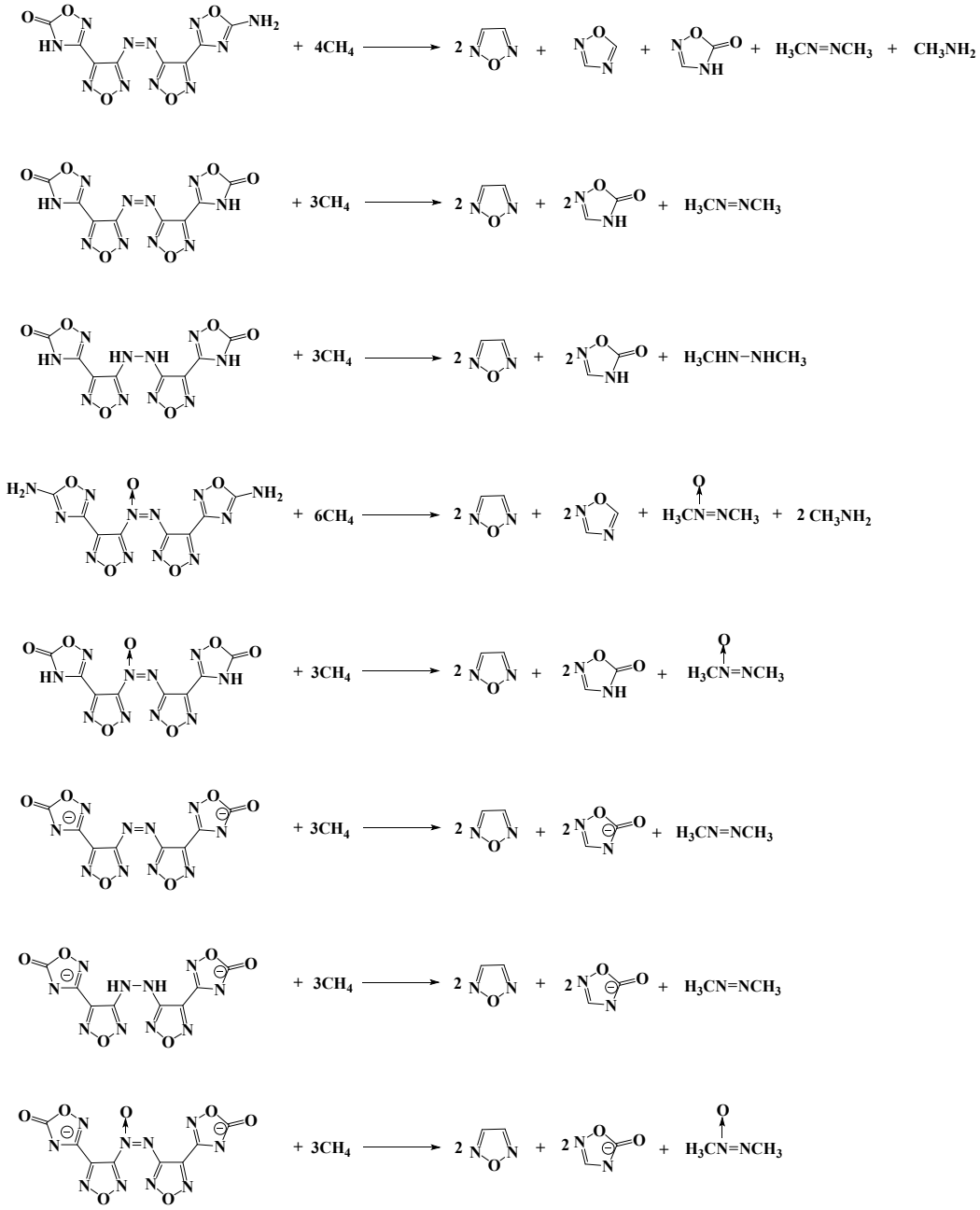



**Figure S19** DSC plot of compound **16**

## Theoretical study

All of the ab initio calculations involved in this work were carried out using the Gaussian 09 suite of programs. The geometric optimization and frequency analyses of the structures are based on available single-crystal structures and using the B3LYP functional with the 6-31++G(d,p) basis set. The geometrical were optimized with no constraints imposed under default convergence criteria. Total energy ($E_0$) and zero-point energy (ZPE) were calculated with vibrational frequency analysis. The heats of formation were obtained by using the isodesmic reaction approach. Atomization energies were obtained by employing the G2 ab initio method. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

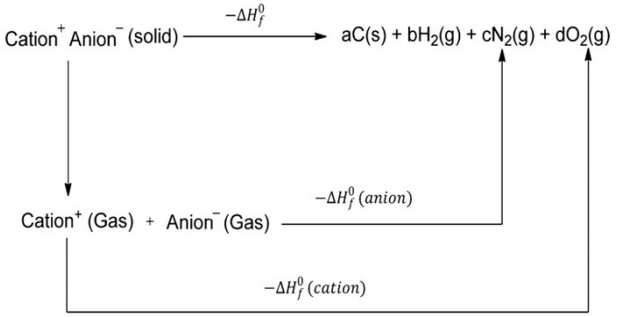


**Scheme S1** Isodesmic reactions for calculating heats of formation for **2**-**4** and **7**-**16**

**Table S11** Enthalpies of the gas-phase species

| Compd | $\Delta H_f$(kJ mol$^{-1}$) |
|---|---|
| 1,2,5-oxadiazole | 196 |
| 1,2,4-oxadiazole | 75 |
| 1,2,4-oxadiazol-5(4H)-one | -125.50 |
| 1,2-dimethyldiazene | 147.85 |
| 1,2,4-oxadiazol-5-one anion | 114.62 |
| methanamine | -23.5 |
| 1,2-dimethylhydrazine | 85.45 |
| methane | -74.6 |
| 1,2-dimethyldiazene oxide | 62.3 |

For energetic salt , the solid-phase heat of formation is calculated on the basis of a Born-Haber energy cycle (Scheme S2). The number is simplified by equation 2:




**Scheme S2** Born−Haber Cycle for the formation of energetic salts

$$\Delta H_f(\text{salt, 298 K}) = \Delta H_f(\text{cation, 298K}) + \Delta H_f(\text{anion, 298K}) - \Delta H_L \quad (1)$$

in which $\Delta H_L$ can be predicted by using the formula suggested by Jenkins, et al.(equation 2):

$$\Delta H_L = U_{pot} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

In this equation, $n_M$ and $n_X$ depend on the nature of the ions $M_p^+$ and $X_q^-$, respectively.

The equation for lattice potential energy $U_{pot}$(equation 3) has the form:

$$U_{POT}\ [\text{kJ mol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

where $\rho_m$ [g cm$^{-3}$] is the density of the salt, $M_m$ is the chemical formula mass of the ionic material, and values for g and the coefficients $\gamma$ (kJmol$^{-1}$cm) and $\delta$ (kJmol$^{-1}$) are assigned literature values.